Synthesis and Mechanical Properties of 3D Nanoporous Graphene Based Materials

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URL	http://hdl.handle.net/10097/00122221

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授　与　学　位	博士（工学）
学位授与年月日	平成２８年９月２６日
学位授与の根拠法規	学位規則第４条第１項
研究科，専攻の名称	東北大学大学院工学研究科（博士課程）知能デバイス材料学専攻
学位論文題目	Synthesis and Mechanical Properties of 3D Nanoporous Graphene Based Materials （3 次元ナノポーラスグラフェン基盤材料の合成と構造評価）
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論文内容要旨

Synthesis and Mechanical properties of 3D Nanoporous Graphene Based Materials (3次元ナノポーラスグラフェン基盤材料の合成と構造評価)

Fabrication and characterization of nanoporous Ni and nanoporous graphene

This study investigates the microstructure-mechanical properties relationships of nanoporous Ni, nanoporous graphene a graphene reinforced metal or polymer composites. Various strategies including microstructure of precursor, dealloyi conditions and post dealloying heat treatment were assessed to enhance the microstructural integrity and improved mechani properties in nanoporous Ni and the properties evaluated through both tensile and indentation testings.

First, Ni30Mn70 ingots were prepared by melting pure Ni and Mn (purity >99.9 at.%) using an Ar-protected arc melti furnace. After annealing at 900°C for 24 hours for microstructure and composition homogenization, the ingots were cold-roll to thin sheets with a thickness of 200, 150 and 50 μm at room temperature. Nanoporous Ni samples were prepared electrochemical dealloying at different conditions or chemical dealloying in a 1.0 M (NH4)2SO4 aqueous solution at 50℃. After dealloying, the samples were rinsed thoroughly with water and ethanol and dried in vacuum.

Methods

Nanotubular graphene preparation

Nanoporous Ni was used as 3D porous and catalytic active substrate to decompose of a carbon source into the carbon atom as a 3D interconnected graphene framework. First, nanoporous Ni (np-Ni) with pore size of 10 nm, prepared by selective dealloying of Ni30Mn70 in 1 M $(NH_4)_2 SO_4$, was loaded into the controllable CVD furnace and annealed at different graphene growth temperature of 800, 900 and 1000ºC under 2500 sccmAr and 100 sccmH_2 for various time. After that, nanotubular graphene was grown into the ligaments surface of annealed nanoporoussamples as a Ni-Graphene core-shell structure (graphene@np-Ni) by introducing a carbon source (benzene). Finally,

3D interconnected hollow nanotubular graphene were fabricated bydissolution of Ni in 3 M HCl acid solution. Nanotubular graphene with tunable density (3-75 mg cm^{-3}) were fabricated by adjusting annealing time before graphene growth between 3minutes to 10 hours (increasing ligament diameter of nanoporous Ni) and graphene growth time from 1 to 10 minutes (increasing graphene layers).

Microstructure characterization

The microstructures were characterized by JEOL JIB-4600F Scaning Electron Microscopy (SEM), JEOL JEM-2100F Transmission Electron Microscopy (TEM) and Raman spectroscopy (Renishaw with an excitation wavelength of 514 nm and laser power of 10 mW).

Mechanical test

Mechanical properties were evaluated by tensile test and microindentation. High precision shimadzu EZ-SX instrument equipped with load cell capacity of 1N and 500N was used to perform tensile test of nt-G and nanoporous Ni at strain rate of $8*10^{-4}$ s^{-1}. Tensile samples were cut into dog bone shape having a gauge length of 6 mm, width of 2 mm and thickness of 35 µm. Indentation experiment was carried out utilizing a nano-microinentation machine (shimadzu W201) using 20 µm spherical tip. Indentation depth was kept lower than 20 µm (10% of sample thickness) to avoid constraint by substrate. Hardness and elastic modulus were extracted from loading-unloading curves using the Field- Swain method.

Results

Chapter 3 (nanoporous Ni): Mechanical properties of nanoporous Ni is reported to be low in tensile loading of bulk samples because of discontinuity and flaws such as cracking which greatly impair interconnectivity of ligaments. As the our priority is to fabricate nanoporous graphene by CVD utilizing nanoporous Ni template whose morphology, connectivity of ligaments and flaws are translatable to the resulting graphene, in this study we set a goal to improve the interconnectivity, mechanical properties of a nonprecious, abundant and cheap structural nanoporous materials emphasizing on tensile improvement. Our results show that, although changing dealloying condition does not improve resistance to cracking, but, engineered precursor alloy with fine grain microstructure is an alternative compared to the coarse grain precursor to distribute interior tensile stress during dealloying and suppress large cracks between coarse grains leading to the micro scale fine cracks. Yield strength of nanoporous Ni from dealloying of fine grain precursor is approached strength of 16 MPa, almost twice as high as yield strength measured for coarse grain one. Post dealloying heat treatment is also a powerful method to remove small fine flaws of nanoporous materials whereas the coarse intergranular cracks are intact even after annealing at high temperature. Enhancement in mechanical properties toward the annealing at high temperature is reached and can be attributed to the ligament connectivity of nanoporous Ni. np-NiF specimens that do not include extended intergranular grain boundaries cracks in as dealloyed or annealed led to the high tensile strength values compared to those measured for coarse grain precursor. The average yield strength value of 117 MPa which was measured during tensile testing of np-NiF annealed at 900 ºC is almost four fold as high as np-NiC is attributed to the removal of fine distributed cracks by annealing and improved

ligament interconnectivity. High ligaments connectivity of np-NiF not only enhanced the mechanical properties, but also make the np-Ni an excellent template to fabricate flaws free nanoporous graphene.

Chapter 3 (Ni-graphene): In this study I also used 3D interconnected bicontinuous graphene as reinforcement to fabricate high strength Ni-graphene metal matrix composites. We used high quality three dimensional interconnected graphene networks as reinforcement instead of isolated graphene sheet or RGO. Interconnected tubular graphene network efficiently prevent graphene aggression during processing as it has been observed in most metal-graphene composite using graphene sheets. The effectiveness of the 3D graphene as reinforcement in UFG-Ni matrix was investigated by performing uniaxial tensile tests at room temperature. A significant strength enhancement is provided by addition of only 2 % (volumetric) of graphene accompanied with superior ductility which is attributable to the ultra-high intrinsic strength of graphene (130 GPa) which is realized by the homogeneous dispersion of graphene network as a continuous reinforcement in the Ni matrix, grain refining originated from grain boundary pinning induced by graphene and high work hardening capability of composites. Extraordinary tensile ductility mainly arises from extensive uniform plastic deformation of Ni-graphene composite before necking as a result of accelerated work hardening capability during tensile loading, which suppose that graphene promote the pinning and accumulation of glide dislocation at the interface compared to the ordinary metal-metal grain boundary.

Chapter 4: The current work represent significant step towards developing ultra-strong tubular graphene foam. However, while all studies have focused on the mechanical behavior of graphene foam and its response to density by compression loading, in the present work, tensile and compression tests were used to study mechanical properties. Mechanical strength of the tubular graphene was significantly enhanced, achieving values similar to those of ceramic microlattice, for instance, modulus and strength of 7 MPa and 420 KPa in compression (2.4 MPa and 250 KPa in tensile loading) at the density of 10 mg cm^{-3}, more than one order higher than all non-covalent graphene foams and much higher than highest value of recently reported for CVD grown nanotubular graphene having modulus and collapse strength of 1.74 MPa and 60 KPa at the density of 9.8 mg cm^{-3}. The emerging single defect free graphene sheet into the 3D entirely interconnected configuration (which benefit from fully interconnected template) allow the foam to profit from covalent strength upon the tensile loading as well as an unprecedented damage tolerance network, resulting in a scaling relationships with the relative density $\bar{\rho}$ as $\mathbf{E}\sim\bar{\rho}^{1.5}$ and $\sigma\sim\bar{\rho}^{1.1}$ ($\sigma\sim\bar{\rho}^{1.5}$ at densities lower than 16 mg cm^{-3}). Excellent mechanical properties could be effectively linked to first; the special morphology of nanoporous Ni template and second to the interconnectivity of template and resulting graphene foam. Failure of tubular structure is a competition of different modes, stretching of tube, bending and shell buckling. Our finding supposes that the low aspect ratio of tubular structure with $(r/l)_{cr}$ = 0.34 higher than transition value 0.103 (originated from low aspect ratio of Ni ligament) precludes the Euler beam buckling and encourage stretching leading to the enhancement in mechanical properties of np-G. Moreover, the wall thickness to radius ratios $(t/r)_{cr}$ are 0.011-0.0232 lower than the transition value of 0.141. Thus, failure mode is determined to be governed by shell buckling mainly at nodes. Results show that, while the low aspect ratio $(r/l)_{cr}$ suppress the Euler buckling of tube and encourage the stretching and high strength,

deformation is dominantly governed by shell buckling, whose degree of buckling depends on the wall thickness determines ductility and stiffening of foam.

Chapter 5: I also used 3D bicontinuous graphene network as a reinforcement and conductive support to enhance mechanical properties and conductivity of a functional polymer; polypyrrole (PPy). I developed a free standing nanotubular hybrid composites with outstanding mechanical robustness while maintain high specific surface area which make it promising for multifunctional application. Mechanical properties of nanotubular PPy and graphene supported PPy were studied by tensile test and micro-indentation in the wide range of densities. It is found that not only mechanical strength and elastic modulus are increased by nanoporous graphene support, but also degradation rate accompanied with lowering density is effectively decreased. Covalently bonded continuous network make the bicontinuous graphene network highly strong and conductive. Effective interface bonding demonstrated by TEM observation enables load transfer capability and enhance conductivity of hybrid which lead to outstanding mechanical properties of low density bicontinuous microstructure. Fabrication of novel composite opens up possibility to develop the light weight high performance hybrid materials for use in electrochemical and electromechanical devices.

論文審査結果の要旨

グラフェンは、１原子の厚みの炭素シートで、高い電気移動度と引張強度を有しているため次世代のエレクトニクス材料として有望視されている。しかし、平滑な単層だけでは応用面で限りがあるため、多孔質化することで二次元の特性を保持しながら、三次元化へ拡張することが重要である。そこで、Kashani Hamzeh 氏は、ナノポーラス金属を基盤とすることで研究を展開した。まず、ナノポーラスグラフェン複合材を作製し、機械特性を包括的に評価した。そして、さらに伝導ポリマー（PPY）とナノポーラスグラフェンを複合化させるプロセスを開発し、靭性強度をさらに向上させることに成功した。論文は６つの章で構成されており、概要は以下のとおりであった。

第１章：ナノポーラス金属の科学的背景

ナノポーラス金属（グラフェン）の作製方法と機械特性について、過去の研究報告と照らしてまとめられた。

第２章：実験方法

本研究で使用した実験機器（TEM, SEM, ラマン分光、硬度試験、引張試験）やそのプロトコル、使用材料について説明した。

第３章：ナノポーラスニッケルとナノポーラスニッケル・グラフェン複合材の作製と機械特性

NiMn 合金から脱成分して作製したナノポーラスニッケルの実験方法の最適化と機械特性について評価した。また、ナノポーラスニッケルの表面に CVD でグラフェンを堆積させ、圧延をして孔をつぶしてナノポーラスニッケル・グラフェン複合材を作製した。作製した複合材は、グラフェンが粒界移動を阻害したため、粒径の高い熱的安定性を有していることが明らかとなった。また、高い靭性を有していた。

第４章：ナノポーラスグラフェンの作製と機械特性

ナノポーラスニッケルの表面に CVD でグラフェンを堆積させ、ニッケルを酸で溶かすことでナノポーラスグラフェンを作製した。密度ｖｓ弾性率のプロットより、これまで報告されていたグラフェン構造材よりも高い弾性率であることが明らかとなった。

第５章：ナノポーラスグラフェン／PPY 複合材の作製と機械特性

ナノポーラスグラフェンを基板として、PPY を電着メッキで複合化させるプロセスを開発した。これにより密度ｖｓ弾性率のプロットにおいて、ナノポーラス PPY よりグラフェンを複合化したものが高い弾性率を示すことが明らかとなった。

第６章：結言

簡潔に結果がまとめられた。

このように、本論文はナノポーラスグラフェンを基軸にした機械特性に関する詳細な検討と結果が示されており、その達成度と独自性は極めて高く評価できる。このような詳細な検討は、Kashani Hamzeh 氏の高い専門知識と独自性により構築・展開されたものであり、研究者としての極めて高い資質を示している。

よって、本論文は博士(工学)の学位論文として合格と認める。